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SYNTHESIS AND CHARACTERIZATION OF SUPERABSORBENT POLYMER COMPOSITES BASED ON ACRYLIC ACID, ACRYLAMIDE AND BENTONITE

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF SUPERABSORBENT POLYMER COMPOSITES BASED ON ACRYLIC ACID, ACRYLAMIDE AND BENTONITE. Superabsorbent polymer (SAP) is a hydrogel material which is capable of absorbing and or storing liquid up to a hundred times of its dry weight. SAP was synthesized from monomers of acrylic acid and acrylamide. Beside that a superabsorbent polymer composite (SAPC) was also made by grafting the SAP with bentonite. The polymerization processes were carried out using a chemical method of a ammonium persulphate (APS) as chemical initiator and N,N-methylene bisacrylamide (MBA) as crosslink forming materials at temperature of 70 ^{o}C in the 500 mL round flask. The homogeneity of the mixture was achieved by an adjustable magnetic stirrer. The result of polymer formed was identified using a FT-IR spectroscopy and the characteristic of absorption was studied using demineral water and 0.9 % NaCl solution. The maximum absorption capacity obtained from SAP is 339 g/g in water and 65 g/g in NaCl solution, while the maximum absorption rate obtained from SPAc is 19.43 g/min in water and 7.3 g/min in NaCl solution. It is interesting to note the absorption characteristic of SAP and SAPc above, the SAP is better in capacity of absorption while the SAPC is better in the rate of absorption. This phenomenon is supported by the result of morphology identification of SEM that shows the micro porous structure of SAP is bigger in number but smaller in pore sizes, while the micro porous structure of SAPC is smaller in number but bigger pore sizes.

Key words : Superabsorbent polymer, Acrylamide, Acrylic acid, Bentonite, Grafting, Absorption capacity

ABSTRAK

SINTESIS DAN KARAKTERISASI KOMPOSIT POLIMER SUPERABSORBEN BERBASIS ASAM AKRILAT, AKRIAMIDA DAN BENTONIT. Polimer superabsorben (*SAP*) merupakan material hidrogel yang mampu menyerap dan/atau menyimpan cairan hingga ratusan kali lipat dari berat keringnya. *SAP* disintesisdari monomer berupa asam akrilat dan akril amida. Kemudian, komposit polimer superabsorben (*SAPC*)-nya dibuat dengan metode *grafting* dari SAP itu dengan bentonit. Proses polimerisasi dilakukan dengan metode kimia yang menggunakan inisiator ammonium persulfat (*APS*) dan *crosslinker* (bahan pemicu *crosslink*) N,N-methylene bisacrylamide (*MBA*) pada suhu 70 ^{o}C dalam sebuah labu 500 mL. Homogenitas dari campuran dicapai dengan memanfaatkan pengaduk magnetik. Polimer yang dihasilkan diidentifikasi dengan spektroskopi *FT-IR* dan sifat absorpsinya dipelajari dengan menggunakan air tanpa mineral (*aqua DM*) serta larutan garam 0,9 % NaCl. Kapasitas absropsi maksimal diperoleh dengan *SAP* ini ialah 339 g/g terhadap air, dan 65 g/g untuk larutan 0,9 % NaCl, sedangkan kecepatan absorpsi maksimal diperoleh dengan *SAPC* 19,43 g/min untuk air dan 7,3 g/min untuk larutan 0,9 % NaCl. Satu hal yang menarik di sini adalah bahwa *SAP* memiliki kapasitas yang lebih baik, sedangkan *SAPC* memiliki kecepatan absorpsi yang lebih baik. Hal ini didukung oleh hasil dari identifikasi morfologi dengan *SEM* yang memperlihatkan bahwa struktur pori mikro dari *SAP* menunjukan jumlah pori-pori yang lebih banyak tetapi ukurannya lebih kecil. Sedangkan pada *SAPC* jumlah pori lebih sedikit, namun dengan ukuran yang lebih besar

Kata kunci : Polimer superabsorben, Akrilamida, Asam Akrilat, Bentonit, *Grafting*, Kapasitas Absorpsi

INTRODUCTION

Superabsorbent polymer (SAP) is a hydrogel material which is capable of absorbing and or storing liquid up to a hundred times of its dry weight. The fluids that can be absorbed by SAP are

water, body fluids such as urine and blood, or other liquids. The advantage of using hydrogel in comparison to other absorbent materials such as paper, cellulose and cotton is the ability of its absorption more than its weight, better in pressure resistant, and it can be described as environmental friendly materials [1,2]. SAP is a polymeric product that can be naturally degraded by microbes to be small molecules such as CO_2, H_2O dan nitrogen and hence safe for use.

The polymer is also sensitive to direct sunlight because it can break the polymer bond and then become some oligomers.The hydrophilicity, swelling in aqueous media, nonsoluble nature in aqueous fluids, and ionic aspect are basic requirements of a good SAP. Because of their unique properties, SAP has a great potential of applications in various systems. For example, since SAP could absorb water in a rainy season and slowly releases it for plants in a dry season, it would help them to survive under dry condition and increases the survival rate of afforestation [4]. Some of their applications include novel moisture sensors, fire protection materials, hygienic products, horticulture, gel actuators, drug delivery systems, as well as water blocking tapes and coal dewatering [5].

However, superabsorbent has negative features in some application fields because of high production cost and low gel strength. To overcome these, inorganic substances can be added as low cost material and a filler to improve the strength properties in the polymer matrixes. In the field of SAP, much attention has recently been paid to a layered silicate in order to improve mechanical properties of SAP by producing a superabsorbent composite (SAPC). Clays, such as kaolin, montmorillonite, and attapulgite have all been used as well in the preparation of SAPC. Pillared clays are modified clays that protect the layered silicate structure [6,7].

In this research, SAP was synthesized from monomers of acrylic acid and acrylamide, while SAPC was made by grafting the SAP with bentonite. Acrylic acid is usually used to produce plastics of homopolymer or copolymer. Acrylamide is a kind of nonionic monomer and has a great advantage as a raw material of SAP due to good salt-resistant. Bentonite is a layered silicate with reactive groups –OH on the surface and was added to SAP in order to reduce costs and improve the properties of compression and rate of its waterabsorbtion. Grafting process carried out by chemical methods, i.e. by using ammonium persulphate (APS) as the initiator and N,N-methylene-bisacrylamide (MBA) as the cross linker. Initiator and cross linker are important components that affect the properties of the final polymerization product.

EXPERIMENTAL METHOD

Materials

Acrylic acid (AA) chemically pure, Merck Factory was distilled under reduced pressure before use. Acrylamide (AM) chemically pure, Merck Factory was used as purchased. Ammonium persulphate (APS) Merck Factory was recrystallized from water. N,N-methylene bisacrylamide (MBA) chemically pure, Merck Factory was used as purchased. Bentonite micro powder (DIY, Indonesia), milled through 320-mesh screen, followed by treatment with 37 % hydrochloric acid for 48 hours and washed with distilled water until pH 7 to remove any residual hydrochloric acid, was dried at 105 ^oC for 8 hours prior to use. All solutions were prepared with distilled water.

Preparation of Superabsorbent

The polymerization of SAP were carried out using a chemical method of a chemical initiator as APS and crosslink forming material as MBA at temperature of 70 ^oC in the 250 mL round flask [8-11]. The homogeneity of the mixture was achieved by an adjustable magnetic stirrer. A series of SAP formulas was prepared by the following procedure: AA (23 mL) was dissolved in 75 mL distilled water and then neutralized with 20.8 mL of sodium hydroxide solution (5 M) in a four-neck flask equipped with a stirrer, condenser and thermometer. AM (10.65 g) and MBA were then added to the above partial neutralized monomer solution. The mixture was stirred at room temperature for about 30 minutes. The water bath was heated slowly to 70 ^oC with effective stirring. After that APS was introduced to the mixed solution and allowed the reaction to take place. 3 hours later, the resulting product was washed several times with distilled water, dried at 70 ^oC to a constant weight, then milled and screened.

Preparation of Superabsorbent Composite

SAPC was prepared in the same way as that of SAP, instead bentonite was also added when MBA was introduced into the 250 mL round flask. The addition of bentonite was varied in order to study the effect of the filler to the properties of SAPC.

Absorption Capacity Measurement

A weighted quantity of the SAP or SAPC was immersed in distilled water or saline solutions at room temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtered over a 100-mesh screen. The absorption capacity (Q_{H_2O}) of superabsorbent composite was determined by weighting the swelled samples, and the Q_{H_2O} of

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the samples was calculated using the following Equation (1) [12] :

$$Q_{H_2O} = \frac{m_2 - m_1}{m_1} \quad \text{..... (1)}$$

Where :

m_1 = Weights of the dry sample
m_2 = Weights of the water-swollen sample
Q_{H2O} = Calculated as grams of water per gram of sample

Absorption Rate Measurement

The absorption rate measurement was done by pouring SAP or SAPC samples (1.0 g, 50-60 mesh) into 10 Erlenmeyer flasks of 1 liter distilled water or desired solution and dispersing them with mild stirring [13]. Then observed the change of sample weight at various interval times by taking out the sample from the flask one by one at consecutive time intervals, and weighted according the procedure above. The absorption rate was obtained from the slope of the curve of sample weight changes against the interval time.

Characterization

The IR spectra of the SAP and SAPC were recorded on a FT-IR-8400 SHIMADZU using KBr pellets. The morphology of the dried samples was examined using a SEM instrument after coating the sample with gold film.

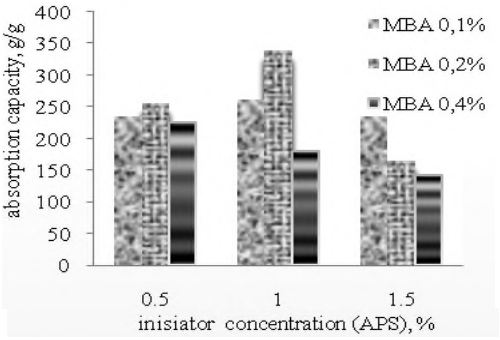

Figure 1. Water absortive capacity of SAP

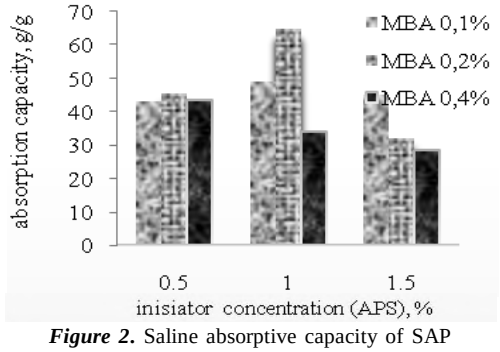

Figure 2. Saline absorptive capacity of SAP

RESULTS AND DISCUSSION

Absorption Characteristics

Absorption capacity of SAP is the ability of SAP to absorb certain liquids by immersing the SAP in the liquid. There are two types of liquid used in determining the absorption capacity i.e. distilled water and 0.9 % NaCl solution. These are the types of fluids expected to represent the application of SAP in the field of agriculture and health such as baby diapers and sanitary napkins.

Figure 1 and Figure 2 show that absorption capacity depends on MBA and salt concentrations. The maximum absorption capacity is obtained at 0.2 % MBA concentration for both distilled water (339 g/g) and saline solution (65 g/g), which means that the density of crosslinking has significant effects on the absorption capacity of SAP. At low crosslinking density (0.1 % MBA), the SAP is weak to hold water molecules and at high crosslinking density the SAP has a little space to accommodate water molecules.

The relationship between absorption capacity of the polymer network structure has been described by Equation (2) as following [14],

$$Q^{5/3} = \frac{(i/2v_u S^{*1/2})^2 + (1/2 - \chi)/V_1}{v_e/V_0} \quad \text{..... (2)}$$

In the Equation (2), the crosslink density is an important element that controls the capacity of the superabsorbent polymer.

Similar trend is shown with the effect of APS concentration, which may indicate that increasing number in short chain SAP will decrease the absorption capacity of SAP. The relationship between absorption capacity and the number of initiators are described by the following Equation (3) [14].

$$v = \frac{[k_p/2v(fk_dk_t)^{1/2}][M]}{[I]^{1/2}} \quad \text{..... (3)}$$

Increasing the amount of the initiator will decrease the polymer molecular weight and increase the number of single polymer chain. Single polymer chain does not contribute to the absorption capacity. Thus the absorption capacity decreases with the increase in the number of initiators. However, if the initiator is too small, the absorption capacity will also decrease. This is because the number of free radicals

Table 1. Water absorptive capacity of SAPC

Variabel		Kapasitas absorbsi, (g/g)					
Jumlah APS (%)		0,5%		1%		1,5%	
MBA (%)	0,1	184,365	A	207,363	B	126,735	C
	0,2	242,690	C	304,085	A	198,589	B
	0,4	165,655	B	187,766	C	208,697	A

A = bentonit concentration 5% ; B = 10% and C = 15%

Table 2. Saline absorptive capacity of SAPC

Variabel		Kapasitas absorbsi, (g/g)					
Jumlah APS (%)		0,5%		1%		1,5%	
MBA (%)	0,1	28,025	A	41,464	B	25,208	C
	0,2	32,545	C	48,112	A	30,612	B
	0,4	26,814	B	30,753	C	36,984	A

A = bentonit concentration 5% ; B = 10% and C = 15%

generated by initiator is small and hence reduces the number of chains formed.

Figures above also show that the present of NaCl reduces a lot the absorption capacity of SAP. This is due to increasing external ionic strength of NaCl, resulting in decrease of osmotic pressure differences between SAP and saline solution.

Table 1 and Table 2 add some more information that increasing concentration of Bentonite in the SAPC will decrease the absorptive capacity of the material. However, the experiment showed that the presence of bentonit in the SAPC increased the rate of water absorption in the beginning, 17 g/g.minutes for 0 % Bentonite and 35 g/g.minutes for 5 % bentonite. This characteristic of SAP and SAPC has opened opportunity of their application, for example SAP may be good for application in agriculture field due to high absorptive capacity while SAPC may be good for application in health field (such as baby diapers) due to fast absorption in the beginning.

FT-IR and SEM Characteristics

Functional group analysis of the sample was carried out using a FT-IR machine and basically done by comparing the absorption band formed in the infrared spectrum using the correlation table [15]. The bentonite FT-IR spectroscopy test result is shown in Figure 3.

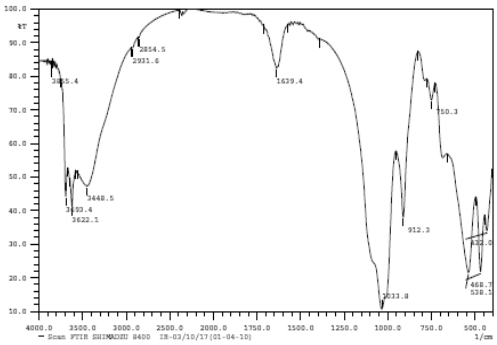

Figure 3. FT-IR spectra of bentonite

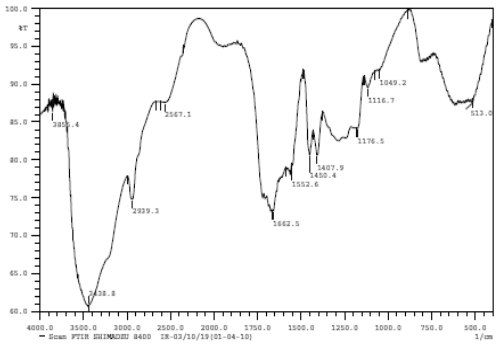

Figure 4. FT-IR spectra of SAP

Table 3. The end groups indentified from SAP sample

Sample	Isolated wave number (cm^{-1})	Theoritical wave number (cm^{-1})	Groups
SAP	3438,8	3310-3500	-OH
	2939,3	2700-3000	-CH
	1662,5	1640-1680	-C=O
	1176,5	1110-1180	$-NH_2$
	1407,9	1350-1470	-NH
	1552,6	1550-1680	-C=O
	1450,4	1400-1480	-NH

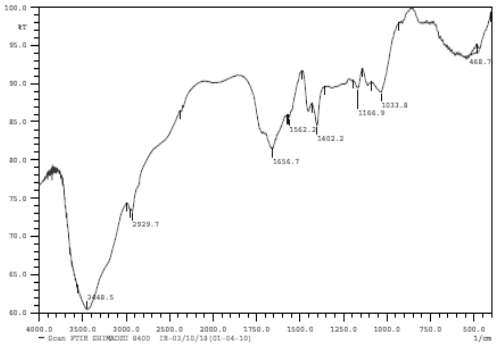

Figure 5. FT-IR spectra of SAPC

Table 4. The end groups indentified from SAP sample

Sample	Isolated wave number (cm^{-1})	Theoritical wave number (cm^{-1})	Groups
SAPC`	3436,9	3310-3500	-OH
	2927,7	2700-3000	-CH
	1656,7	1550-1680	-C=O
	1164,9	1110-1180	$-NH_2$
	1402,2	1350-1470	-NH
	1562,2	1550-1680	-C=O
	1033,8	685-1040	Si-O (bentonite)

It can be seen from Figure 3 that the infra-red spectrum of bentonite are on the wave number 3622.1, which refers to -OH groups, and the wave number 1033.8, which refers to Si-O clusters. These two groups, -OH and Si-O, are the main characteristics of bentonite, which has the sharpest intensity band.

Figure 4 shows the FT-IR spectroscopy result of SAP. All wave numbers representing groups in the SAP are given in Table 3. There are 7 groups identified in the spectrum, i.e. -OH group originally from AA monomer, $-NH_2$ group from AM monomer, -CH and -C=O groups from AA and AM monomers, and -NH group from MBA cross linker. These are all hydrophilic groups that make the polymer having high capability of absorbing water or saline solution.

Figure 5 shows the infra-red spectrum of SAPC. All wave numbers representing groups in the SAPC are given in Table 4. This FT-IR spectrum of SAPC clearly shows that the material is combination between SAP and bentonite, as indicated by the regional SAPC of 1033.8 wave number which is a characteristic absorption of Si-O clusters derived from bentonite.

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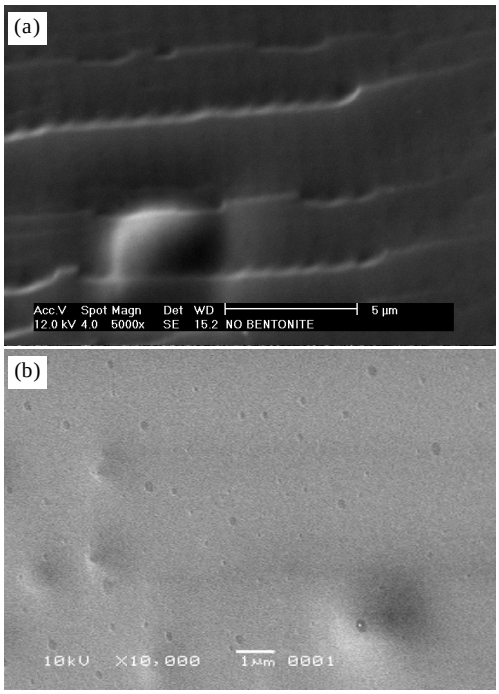

Figure 6. Scanning electron micrographs of SAP (a). 5000x and (b). 10.000x

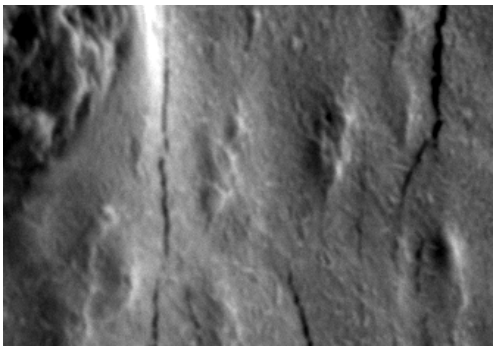

Figure 7. Scanning electron micrographs of SAPC 5000x

SAP and SAPC morphologies were identified by SEM in order to analyze the surface and micro pore of the material. The morphology is believed to have an effect on the absorptive characteristics of SAP and SAPC, either on their absorptive capacity or absorptive rate. The surface and micro pore are places where water and saline solution interact with hydrophilic groups. Hence, their form and number are important to observe.

Figure 6 shows the surface microstructure of SAP is very smooth, having many small pores (200-230 nm). This has made SAP having a higher absorptive capacity but a slower absorptive rate compared to those of SAPC. Further look to the surface of SAPC in Figure 7, the surface looks rough and has many strains, which indicate that the surface area and pore cavities of SAPC are larger than those of SAP. This may contribute to the faster absorption rate of SPAC. Additionally, bentonite of SAPC may cause many small pores closed and hence reduce its absorptive capacity.

CONCLUSIONS

This research has already showed that superabsorbent polymer (SAP) and superabsorbent polymer composite (SAPC) synthesized using chemical method of MBA cross linker and APS initiator having good absorptivity, which are significantly different between those in distilled water and saline solution. In addition, introduction of bentonite to the SAP can produce SAPC that has faster absorptive rate in the beginning and slightly lower absorptive capacity than SAP has. Therefore, SAP may suitable for application in agriculture area and SAPC in health area.

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